

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6 : A61K 7/06</p>	<p>A1</p>	<p>(11) International Publication Number: WO 96/31188 (43) International Publication Date: 10 October 1996 (10.10.96)</p>
<p>(21) International Application Number: PCT/EP96/01462 (22) International Filing Date: 1 April 1996 (01.04.96) (30) Priority Data: 9507130.4 6 April 1995 (06.04.95) GB (71) Applicant (for AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: BIRTWISTLE, David, Howard; 13/5 Sukhumvit Soi 49-4, Klongtoey, Bangkok 10110 (TH). MURRAY, Andrew, Malcolm; 15 Moorings Close, Parkgate, South Wirral, Cheshire L64 6TL (GB). (74) Agent: MULDER, Cornelis, Willem, Reinier, Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: HAIR TREATMENT COMPOSITIONS</p> <p>(57) Abstract</p> <p>Hair treatment compositions which can generate style benefits while giving good conditioning comprise a non-rigid, emulsion polymerised cross-linked silicone conditioning polymer having from about 0.05 % to about 10 % branched monomer units.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

HAIR TREATMENT COMPOSITIONS

Field of Invention

5 The invention relates to hair treatment compositions containing particular types of silicones which can generate style benefits while giving good conditioning.

Background of Invention and Prior Art

10 The use of silicones as conditioning agents in hair treatment compositions is well known and widely documented in the patent literature. However, a problem associated with such materials is that their use at levels necessary
15 for achieving good tactile and/or visual benefits can make the hair too soft to style or retain a style. Fine hair in particular can appear limp and unmanageable.

 Accordingly, stylability is generally achieved by
20 application of film-forming materials to the hair, usually after shampooing and/or conditioning, in the form of mousses, gels or sprays. However, the adhesive and/or resinous materials used frequently for style retention can damage dry hair properties, especially hair feel and ease
25 of dry combing. Also, many people require a degree of stylability improvement without the inconvenience and cost of a separate step.

 Highly viscous silicones have the ability to modify the
30 condition and manageability of hair. Siloxane gums improve the combability, softness and condition of the hair and reduce its susceptibility to damage due to mechanical manipulation caused for example by brushing and styling. Silicone resins give body to fine, limp hair and
35 increase the ability of hair to hold a style.

- 2 -

EP-A-240 350 and US 4902499 (Procter & Gamble) for example disclose the use of specific rigid silicone polymers dissolved in a volatile carrier material for giving improved style retention to hair. The polymers described are incorporated in the form of an aqueous silicone emulsion comprising an anionically stabilised hydroxylated polyorganosiloxane, colloidal silica and a catalyst, which crosslinks to form an elastomer on the hair when the water content dries out. Also mentioned are siloxanes, which are required to be soluble in solvents such as cyclomethicone.

EP-A-0 468 721 (Unilever) describes how highly viscous silicones are extremely difficult to incorporate into a shampoo product because they cannot themselves be dispersed to form droplets or an emulsion and must first be dissolved in a volatile solvent, such as a volatile silicone.

The need to use solvents or carriers is disadvantageous for several reasons. For example, products obtained through the use of such solvents or carriers are prone to significant thinning, thereby making it necessary to use a thickening agent to provide a product of commercially and aesthetically acceptable viscosity. Furthermore, volatile organic solvents or carriers generally act as foam suppressors and therefore impair the foamability and ease of spreading of products, especially shampoos, containing them. They can also affect the conditioning properties of the silicone and their volatility can cause safety hazards during processing.

EP-A-0445982 (Dow Corning) discloses the use for hair conditioning purposes of emulsion polymerised highly branched and crosslinked polydimethylsiloxane (including less than about 40% of linear silicone polymer) in a

- 3 -

hydrophobic cationic emulsion. EP-A-0381318 (Dow Corning) discloses hair conditioning compositions comprising certain polydiorganosiloxane-polyoxalkylene copolymers, not in the form of emulsion polymers.

5

Our copending application PCT/EP94/03233 (WO95/09599) describes hair conditioning shampoo compositions containing non-volatile insoluble dimethiconol nonionic conditioning polymer which is emulsion polymerised, thereby obviating the need for an organic solvent for the gum. The specification refers in passing to the possibility of the dimethiconol polymer being cross-linked but there is no discussion and no examples of this and no appreciation of the styling benefits of cross-linking. Emulsion polymerised silicones as such are known from US 2 891 920 (Hyde), US 3 294 725 (Findlay) and US 3 360 491 (Axon).

We have now found that emulsion polymerised silicones which are cross-linked in the emulsion form give improved styling benefits without compromising conditioning properties when formulated into a hair treatment composition. Cross-linking in emulsion form gives more precise control of the level of cross-linked silicone deposited on the hair compared with systems which cross-link during drying onto the hair, and greater ease of formulation compared with systems which employ an organic solvent or carrier of the silicone.

30 Definition of the Invention

The present invention provides a hair treatment composition comprising a non-rigid emulsion polymerised cross-linked silicone conditioning polymer, in which the polymer has from about 0.05% to about 10% branched monomer units.

35

Detailed Description of the Invention

5 The non-rigid emulsion-polymerised cross-linked silicone conditioning polymer is preferably present in compositions of the invention in an amount from about 0.01% to about 50% by weight based on the total weight of the composition, more preferably from about 0.1 to about 20% by weight, most preferably from about 0.3 to about 10% by weight.

10 Preferred silicone conditioning polymers for use in the invention are polydiorganosiloxanes, preferably derived from suitable combinations of $R_3SiO_{0.5}$ units and R_2SiO units where each R independently represents an alkyl, alkenyl
15 (e.g., vinyl), alkaryl, aralkyl, or aryl (e.g. phenyl) group. R is most preferably methyl.

The preferred silicone conditioning polymers of the invention are cross-linked polydimethyl siloxanes (which
20 have the CTFA designation dimethicone), optionally having end groups such as hydroxyl. Good results have been obtained with dimethicone.

Cross linking of the silicone conditioning polymer is
25 typically introduced concurrently during emulsion polymerisation of the polymer through the inclusion of the required amount of trifunctional and tetrafunctional silane monomer units, for example, those of formula $R Si (OH)_3$ wherein R represents an alkyl, alkenyl (e.g.
30 vinyl), alkaryl, aralkyl or aryl (e.g. phenyl) group, preferably methyl.

The degree of cross-linking of the silicone conditioning polymer can be measured as the percentage of branched
35 monomer units in the silicone conditioning polymer and is suitably from about 0.05% to about 10%, preferably being

- 5 -

in the range about 0.15 to about 7%, e.g., from about 0.2% to about 2%. Increasing cross-linking is found to improve styling benefits but also to reduce conditioning performance somewhat, so compromise levels must be selected with properties optimised to suit consumer preferences in different cases. Good overall performance has been obtained with dimethicone 0.6% cross-linked.

Suitable emulsion polymerised cross-linked silicone conditioning polymers are commercially available or can be readily made using conventional techniques well known to those skilled in the art.

Advantageously, the viscosity of the silicone conditioning polymer is at least 10^6 cst to give good styling benefits and preferably does not exceed 10^9 for ease of formulation.

Preferably, the average particle size of the silicone material of the silicone conditioning polymer is less than 20 microns, more preferably less than 2 microns. Small particle size enables a more uniform distribution of silicone conditioning polymer on the hair for the same concentration of silicone in the hair treatment composition described. Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments.

Hair treatment compositions according to the invention may suitably take the form of shampoos, conditioners, sprays, mousses or lotions. Particularly preferred forms are shampoos, conditioners and mousses, including "3-in-1" styling shampoos, having cleaning, conditioning and styling properties.

A preferred hair treatment composition in accordance with the invention is a shampoo composition which, in addition

to the silicone conditioning polymer comprises (further) surfactant to provide a deterging benefit. The deterging surfactant is selected from anionic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

5

Suitable anionic surfactants include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

20

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

30

Nonionic surfactants suitable for use in compositions of the invention may include condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene

35

- 7 -

oxide groups. Other suitable nonionics include mono- or di-alkyl alkanolamides. Example include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

5 Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates,
10 alkylamphoglycinates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl
15 betaine and sodium cocamphopropionate.

The surfactants are present in shampoo compositions of the invention in an amount of from 0.1 to 50% by weight, preferably from 0.5 to 30% by weight.

20 Hair treatment compositions in accordance with the invention may also take the form of hair conditioning compositions, which preferably comprise one or more cationic surfactants. The use of cationic surfactants is
25 especially preferred, because these ingredients are capable of providing conditioning benefits to hair.

Examples of cationic surfactants include:

30 quaternary ammonium hydroxides, e.g., tetramethylammonium hydroxide, alkyltrimethylammonium hydroxides wherein the alkyl group has from about 8 to 22 carbon atoms, for example octyltrimethylammonium hydroxide, dodecyltrimethyl-
35 ammonium hydroxide, hexadecyltrimethylammonium hydroxide, cetyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethyl-

- 8 -

benzylammonium hydroxide, stearyl-di-methylbenzylammonium
hydroxide, didodecyldimethylammonium hydroxide,
dioctadecyldimethylammonium hydroxide, tallow
trimethylammonium hydroxide, cocotrimethylammonium
5 hydroxide, and the corresponding salts thereof, e.g.,
chlorides
Cetylpyridinium hydroxide or salts thereof, e.g., chloride
Quaternium -5
Quaternium -31
10 Quaternium -18
and mixtures thereof.

In hair conditioning compositions according to the
invention, the level of cationic surfactant is preferably
15 from 0.01 to 10%, more preferably 0.05 to 5%, most
preferably 0.1 to 2% by weight of the composition.

Hair treatment compositions of the invention may also
contain one or more additional conditioning agents,
20 preferably selected from cationic polymers, protein
hydrolyzates and quaternised protein hydrolysates.

Suitable cationic polymers include:
Guar hydroxypropyltrimmonium chloride
25 Poly(dimethyldiallylammonium chloride)
Poly(dimethylbutenyl ammonium chloride) -a,w-
bis(triethanolammonium chloride)
Poly(dipropyldiallylammonium chloride)
Poly(methyl-B-propaniodiallylammonium chloride)
30 Poly(diallylpiperidinium chloride)
Poly(vinyl pyridinium chloride)
Quaternised poly (vinyl alcohol)
Quaternised poly (dimethylaminoethylmethacrylate)
Poly-Quaternium 7
35 Poly-Quaternium 10
Poly-Quaternium 11

- 9 -

Poly-Quaternium 22
Poly-Quaternium 16
and mixtures thereof.

5 Suitable protein hydrolysates include lauryl dimonium
hydroxy propylamino hydrolysed animal protein, available
commercially under the trade name LAMEQUAT L, and
hydrolysed keratin containing sulphur-bearing amino acids,
available commercially under the trade name CROQUAT WKP.

10 A further optional component of hair treatment
compositions of the invention is a deposition aid,
preferably a cationic deposition polymer.

15 The cationic deposition aid will generally be present at
levels of from 0.001 to 5%, preferably from about 0.01 to
1%, more preferably from about 0.02% to about 0.5% by
weight. The polymer may be a homopolymer or be formed
from two or more types of monomers. The molecular weight
of the polymer will generally be between 5 000 and 10 000
20 000, typically at least 10 000 and preferably in the
range 100 000 to about 2 000 000. The polymers will have
cationic nitrogen containing groups such as quaternary
ammonium or protonated amino groups, or a mixture thereof.

25 The cationic charge density has been found to need to be
at least 0.1 meq/g, preferably above 0.8 or higher. The
cationic charge density should not exceed 4 meq/g, it is
preferably less than 3 and more preferably less than 2
meq/g. The charge density can be measured using the
30 Kjeldahl method and should be within the above limits at
the desired pH of use, which will in general be from about
3 to 9 and preferably between 4 and 8.

35 The cationic nitrogen-containing group will generally be
present as a substituent on a fraction of the total
monomer units of the cationic deposition polymer. Thus

- 10 -

when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition.

5

Suitable cationic deposition aids include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

15

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

20

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

25

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkyl aminoalkyl acrylate, dialkylamino alkylmethacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidine, e.g., alkyl vinyl imidazolium, and quaternized pyrrolidine, e.g., alkyl

30

35

- 11 -

vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidine salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁-C₃ alkyls, more preferably C₁ and C₂ alkyls.

5

Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁-C₇ hydrocarbyls, more preferably C₁-C₃ alkyls.

10

The cationic deposition aids can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

15

Suitable cationic deposition aids include, for example: copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g., Chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA" as Polyquaternium-16) such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially from Gar Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymer including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; mineral acid salts of amino-alkyl esters of homo- and copolymers of unsaturated carboxylic acids having from 3 to

20

25

30

35

- 12 -

5 carbon atoms, as described in U.S. Patent 4,009,256; and cationic polyacrylamides as described in our copending UK Application No. 9403156.4 (WO95/22311).

5 Other cationic deposition aids that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

10 Cationic polysaccharide polymer materials suitable for use in compositions of the invention include those of the formula:



20 wherein: A is an anhydroglucose residual group, such as starch or cellulose anhydroglucose residual,

R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,

25 R^1 , R^2 and R^3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R^1 , R^2 and R^3) preferably being about 20 or less, and X is an anionic counterion ,
30 as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl
35 cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as

- 13 -

Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are
5 available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other cationic deposition aids that can be used include
10 cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (Commercially available from Celanese Corp. in their Jaguar trademark series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g.. as described in U.S. Patent
15 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

20 As discussed above, the cationic deposition aid is water soluble. This does not mean, however, that it must be soluble in the hair treatment composition. Preferably, however, the polymer is either soluble in the composition, or in a complex coacervate phase in the composition,
25 formed by the polymer and anionic material. Complex coacervates of the polymer can be formed with anionic surfactants or with anionic polymers that can optionally be added to the compositions of the invention (e.g., sodium polystyrene sulfonate).

30 Coacervate formation is dependent upon a variety of criteria such as molecular weight, concentration, and ratio of interacting ionic materials, ionic strength (including modification of ionic strength, for example, by
35 addition of salts), charge density of the cationic and anionic species, pH, and temperature.

- 14 -

It is believed to be particularly advantageous for the cationic deposition aid to be present in the composition in a coacervate phase, or to form a coacervate phase upon application or rinsing of the composition to or from the hair. Complex coacervates are believed to more readily deposit on the hair. Thus, in general, it is preferred that the deposition aid exist in the composition as a coacervate phase or form a coacervate phase upon dilution. If not already a coacervate in the composition, the deposition aid will preferably exist in a complex coacervate form in the composition upon dilution with water to a water: composition weight ratio of about 20:1, more preferably at about 10:1, even more preferably at about 8:1.

Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the composition.

Preferably the deposition aid is selected from the group comprising cationic polyacrylamides, hydroxyalkyl cellulose ethers and cationic guar derivatives. Particularly preferred deposition aids are Jaguar C13S with a cationic charge density of 0.8meq/g. Jaguar C13S is guar hydroxypropyltrimonium chloride. Other particularly suitable materials include Jaguar C15, Jaguar C17 and Jaguar C16 and Jaguar C162, A preferred cellulose ether is Polymer JR400.

35

- 15 -

The composition may further comprise from 0.1 to 5 % of a silicone suspending agent selected from selected from polyacrylic acids cross linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, 5 copolymers of carboxylic acid- containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol 10 stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Ethylene glycol distearate and Polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or 15 Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used, they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a 20 monomer and acrylic acid esters is Carbopol 1342. All Carbopol materials are available from Goodrich and Carbopol is a trade mark.

Suitable cross linked polymers of acrylic acid and 25 acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

Another ingredient that may advantageously be incorporated 30 into hair treatment compositions of the invention is a fatty alcohol material. The use of such materials is especially preferred in conditioning compositions of the invention, in particular conditioning compositions which 35 comprise one or more cationic surfactant materials. The combined use of fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be

- 16 -

especially advantageous, because this leads to the formation of a lamellar phase, wherein the cationic surfactant is dispersed.

5 Preferred fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 20. Examples of preferred fatty alcohols are cetyl alcohol and stearyl alcohol. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of
10 compositions of the invention.

The level of fatty alcohol materials is conveniently from 0.01 to 10%, preferably from 0.1 to 5% by weight of the composition. The weight ratio of cationic surfactant to
15 fatty alcohol is preferably from 10:1 to 1:10, more preferably from 4:1 to 1:8, most preferably from 1:1 to 1:4.

Hair treatment compositions in accordance with the invention may also take the form of aerosol foams
20 (mousses) in which case a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hair mousse character.

25 The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Examples of suitable propellants include dimethyl ether, propane, n-butane and isobutane, used singly or in admixture.

30 The amount of the propellant gases is governed by normal factors well known in the aerosol art. For hair mousses, the level of propellant is generally from about 3% to about 30%, preferably from about 5% to about 15% of the
35 total composition.

- 17 -

Small quantities of surfactant ranging anywhere from 0.1 to about 10%, preferably from about 0.1 to about 1%, most preferably about 0.3% by weight may be present in the hair mousse compositions of the invention. The surfactant may
5 be an anionic, nonionic or cationic emulsifier. Particularly preferred are nonionic emulsifiers which are formed from alkoxylation of hydrophobes such as fatty alcohols, fatty acids and phenols.

10 Depending on the type of composition employed, one or more additional ingredients conventionally incorporated into hair treatment compositions may be included in compositions of the invention. Such additional ingredients include styling agents, such as resins and
15 hair-setting polymers, perfumes, dyes, buffering or pH adjusting agents, viscosity modifiers, opacifiers, pearlescers, preservatives, antibacterial agents, antidandruff agents, foam boosters, proteins, moisturising agents, herb or other plant extracts and other natural
20 ingredients.

The invention is further illustrated by way of the following non-limitative examples:

25 Example 1

A shampoo composition was prepared by mixing the following components in the amounts stated.

30	<u>Component</u>	<u>% by weight</u>
	Sodium lauryl ether sulphate 2EO	16.0
35	Cocamidopropyl betaine	2.0
	Jaguar C13S	0.2
	CARBOPOL 980	0.4

- 18 -

	Silicone ⁽¹⁾	3.3
	Preservative, colour, fragrance	q.s.
5	Water	to 100%

(1) Emulsion polymerised dimethicone containing 0.6% cross-linking, 60% aqueous emulsion, ex Dow Corning.

The silicone is non-rigid, has a viscosity of 8×10^7 cps and a particle size of 0.5 microns.

In this and the following Examples, the % of cross-linking of the silicone refers to the % of branched monomer units in the silicone.

25

Example 2

A shampoo composition was prepared by mixing the following components in the amounts stated.

	<u>Component</u>	<u>% by weight</u>
35	Sodium lauryl ether sulphate 2EO	8.0
	Cocamidopropyl betaine	4.0
	Jaguar C13S	0.1
40	EUPERLAN PK3000 ⁽²⁾	8.0
	Silicone ⁽³⁾	3.3
45	Preservative, colour, fragrance	q.s.
	Water	to 100

(2) Mixture of SLES 4EO, glycol distearate and cocamidopropyl betaine, ex Henkel

- 19 -

(3) Non-rigid emulsion polymerised dimethicone containing 1.8% cross-linking, 60% aqueous emulsion, ex Dow Corning.

5 The shampoo compositions of Examples 1 and 2 act to clean, condition and style hair. The surfactant (sodium lauryl ether sulphate 2EO) cleans the hair and the cross-linked silicone conditions and styles.

Example 3

10

A hair conditioning composition was prepared by mixing the following components in the amounts stated.

	<u>Component</u>	<u>% by weight</u>
15	Cetyl trimethylammonium chloride	0.7
20	Cetostearyl alcohol	1.2
	Glyceryl monostearate	0.7
	Paraffin wax	1.0
25	Silicone ⁽⁴⁾	3.3
	Preservative, colour, fragrance	q.s.
30	Water	to 100%

(4) As in Example 1

35

Example 4

A hair mousse was prepared by mixing the following components in the amounts stated.

40	<u>Component</u>	<u>% by weight</u>
	Silicone ⁽⁵⁾	1.0

- 20 -

	EMPILAN NP9 ⁽⁶⁾	0.3
	Butane/propane	5.5
5	Preservative, fragrance	q.s.
	Water	to 100

10 ⁽⁵⁾ As in Example 1

⁽⁶⁾ Nonyl phenol ethoxylate 9EO, ex Albright & Wilson

15 The compositions of Examples 1 to 4 gave both styling and conditioning benefits to hair.

20 The styling and conditioning performance of a shampoo composition with the formulation as in Example 1, and variants including silicones with different percentages of cross-linking, and also a non cross-linked silicone emulsion polymer (referred to as X2-1784) as disclosed in Example 2 of WO95/09599 were tested in the following Examples.

25 Example 5

Measurement of styling in vitro

30 This test measures the development of curl in hair switches.

a) Switch Preparation

35 Ten grams of hair was prepared into switches. Six such switches were then layered (removing 2g hair) and permed around 6 x 1cm rollers using a perm kit.

b) Switch Treatment

- 21 -

The switches were split into two groups of three and one group was washed twice for 30 secs with 1 g of shampoo and rinsed for 60 secs. The other group was washed in the same way with another shampoo for comparison. The switches were then scrunched dry with fingers and dried with a hairdryer to generate curls.

c) Evaluation

- After styling the switches were ranked by a team of 12 trained panellists for perm drop (the panellists' perception of the total length of the main body of the switch) on a scale of 1 to 6.
- The average score for each switch was calculated, then the average score for each treatment was calculated. The total score for the two treatments being compared is always 7, with the maximum split being 5-2. The results are expressed as relative perm drop, i.e. product 1 score - product 2 score. A positive result means that product 1 is better than product 2, with a score of +3.0 (5-2) being the maximum score. Results were as follows.

Level of cross-linker	Perm Drop (1 - 2)
0.15 v 0.0	2.0
0.6 v 0.0	3.0
0.6 v 0.15	3.0
0.6 v 1.8	1.0
0.6 v 7.0	-3.0
0.6 v X2-1784	3.0

The results show that the cross-linked silicone gives a styling benefit over uncross-linked silicone and also over the X2-1784 non cross-linked conditioning emulsion polymer

- 22 -

as described in WO95/09599. The results also show that increasing the percentage of cross-linking improves the styling performance.

5 Example 6

Conditioning performance

10 The condition of the switches after washing in the shampoos used in Example 5 was measured by dry combing as follows.

15 7g of hair in the form of a switch was worked in 0.7g shampoo, lathered for 30 seconds, and rinsed with water. The procedure was repeated once. Three switches of hair were prepared for each product to be evaluated. The evaluation of dry combing was carried out by twelve trained pannelists as a paired comparison test and significant differences at greater than 95% confidence was assessed. Results are shown in the following table, with each row including entries for two shampoos being compared in the form of relative allocation of a total score of 100, a higher score indicating preference for that member of the pair.

25

X2-1784	0%XL	0.15%XL	0.6%XL	1.8%XL	7.0%XL
72	28*				
	85	15*			
		51	49		
		76		24*	
		68			32*

30

* indicates results significantly different at greater than 95% confidence level.

- 23 -

The results show that conditioning deteriorates as cross linking increases; thus there is a trade off between conditioning and styling. The optimum will depend on consumer preference.

5

Example 7

10 The shampoo of Example 1 (0.6% cross-linked silicone) was compared with a control silicone based conditioning shampoo sold in the UK under the trade name "PANTENE 2 in 1". The compositions were used to treat identical hair switches which were then subjected to a series of paired comparison tests by trained panellists. The two
15 attributes considered to be most indicative of conditioning benefit are (a) ease of dry combing and (b) smooth feel of the hair when dry.

The shampoo of Example 1 was found to be at least as good as the control in both tests.

CLAIMS

1. A hair treatment composition comprising a non-rigid, emulsion-polymerised cross-linked silicone conditioning polymer, in which the polymer has from about 0.05% to about 10% branched monomer units.
2. A composition according to claim 1, in which the silicone conditioning polymer is a cross-linked dimethicone.
3. A composition according to claim 1 or 2, in which the silicone conditioning polymer has from about 0.15% to about 7% branched monomer units.
4. A composition according to any one of the preceding claims, in which the viscosity of the silicone conditioning polymer lies in the range 10^6 to 10^9 cst.
5. A composition according to any one of the preceding claims, in which the average particle size of the silicone conditioning polymer is less than 20 microns.
6. A composition according to any one of the preceding claims, which is a hair styling composition.
7. A composition according to any one of the preceding claims, which is a shampoo containing from about 0.1 to about 50% by weight of one or more surfactants chosen from anionic, nonionic or amphoteric surfactants or mixtures thereof.
8. A composition according to any one of the preceding claims, which is a conditioning composition containing one or more conditioning agents.

- 25 -

9. A composition according to any one of the preceding claims, comprising a deposition aid and/or a fatty alcohol material.
- 5 10. A composition according to claim 9, comprising from about 0.01 to about 5% by weight of a deposition aid which is a cationic polymer selected from the group comprising hydroxyalkyl cellulose ethers, cationic guar derivatives and cationic polyacrylamides.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 96/01462

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO,A,95 09599 (UNILEVER PLC ;UNILEVER NV (NL)) 13 April 1995 cited in the application see claims see page 8, line 21 - line 26 ---	1,2,4,5, 7-10
A	EP,A,0 445 982 (DOW CORNING) 11 September 1991 cited in the application see examples ---	1,2,8
A	EP,A,0 268 982 (TORAY SILICONE CO) 1 June 1988 see page 2, line 22 - line 39 see page 4, line 16 - line 39 --- -/--	1,2,5-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

27 August 1996

Date of mailing of the international search report

02-09-1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

McConnell, C

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 96/01462

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP,A,0 529 883 (UNILEVER PLC ;UNILEVER NV (NL)) 3 March 1993 see page 2, line 41 - line 59 see page 3, line 41 - line 59 -----</p>	1,5,7-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/01462

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9509599	13-04-95	AU-B- 7810594 EP-A- 0722309	01-05-95 24-07-96
EP-A-0445982	11-09-91	US-A- 5049377 CA-A- 2036444 DE-D- 69101069 DE-T- 69101069 JP-A- 5092912	17-09-91 03-09-91 10-03-94 11-08-94 16-04-93
EP-A-0268982	01-06-88	JP-B- 4062288 JP-A- 63130512 AU-B- 615423 AU-B- 8327187 DE-A- 3777763 WO-A- 8803792	05-10-92 02-06-88 03-10-91 16-06-88 30-04-92 02-06-88
EP-A-0529883	03-03-93	AU-B- 651236 AU-B- 2104092 CA-A- 2075767 JP-A- 5194142 JP-B- 7080740 ZA-A- 9206141	14-07-94 18-02-93 17-02-93 03-08-93 30-08-95 14-02-94